Journal of Organometallic Chemistry, 411 (1991) 107–120
Elsevier Sequoia S.A., Lausanne
JOM 21757

On the Lewis acid-catalysed reaction of the 2,3-bis(trimethylstannyl)-1-alkene moiety with aldehydes

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(Received January 10th, 1991)

Abstract

Compounds containing the 2,3-bis(trimethylstannyl)-1-alkene moiety react with aldehydes in the presence of boron trifluoride etherate to give homoallylic alcohols in which the remaining vinylic stannyl moiety has undergone halodemethylation. A mechanistic explanation for this behaviour is presented. NMR studies indicate that the addition proceeds in an *erythro*-selective manner.

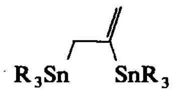
Introduction

The addition reaction between allyltin compounds and aldehydes has been known for over 20 years, the first reported example [1] being the following:

$$H_2C{=}CHCH_2SnEt_3 + RCHO \xrightarrow{200\,^{\circ}C} H_2C{=}CHCH_2CHR(OSnEt_3)$$

Such reactions have been the subject of a very large number of investigations: while early work dealt with reactions at high temperature [2–4], high pressure was later used to promote the reaction [5]. However, most of the work published has made use of Lewis acids to catalyse the reactions [6], the catalysts used including $SnCl_4$ [7,8], $TiCl_4$ [8], $ZrCl_4$ [8] and $CoCl_2$ [9]. The disadvantages common to these compounds, in particular low stereoselectivity, can be avoided [10–12] by the use of boron trifluoride etherate. Yamamoto has recently reviewed this area of tin chemistry [13]. The continued interest in this type of reaction can be seen in the fact that a very recent *Tetrahedron* "Symposium-in-Print" contained no less than four articles dealing with the allyltin/aldehyde reaction [14–17].

Palladium-catalysed additions of ditins to allenes [18] afford compounds containing the structural unit



in which one allylic and one vinylic tin moiety is present. We have carried out reactions of compounds of this type with aldehydes in the presence of $BF_3 \cdot Et_2O$ in order to test their synthetic efficacy, since they have the advantage of containing a

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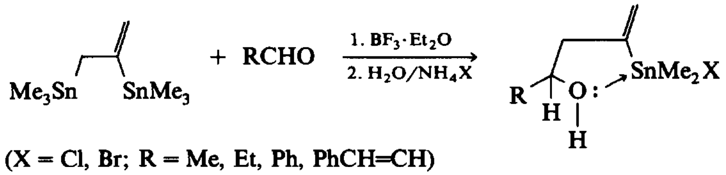
second, less reactive, R_3Sn group that can subsequently be used for further synthetic elaboration of the products.

Results and discussion

Reactions of 2,3-bis(trimethylstannyl)-1-propene

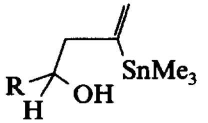
This molecule, obtained by reaction of Me_6Sn_2 with allene or propyne in the presence of $Pd(PPh_3)_4$, can be considered as a model compound since allylic rearrangement will not complicate its reactions. Details of these, which were carried out by procedures described by Tagliavini [19] and Yamamoto [20], are given in Table 1.

The most surprising feature of the reaction is that aldehyde addition is accompanied by halodemethylation at the vinylic tin, the halogen atom incorporated originating from the ammonium chloride/bromide used in the work-up:

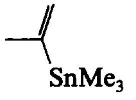


(X = Cl, Br; R = Me, Et, Ph, PhCH=CH)

Additional products detected are:



and



The latter will be referred to below as the "hydrolysis product". In one case 10% of the aldehyde trimer $[(EtCHO)_3]$ was obtained, although dissociation of the trimer is sugested to occur above −40 °C [21].

Table 1

Reactions of $Me_3SnCH_2C(SnMe_3)=CH_2$ with aldehydes RCHO catalysed by $BF_3 \cdot Et_2O$

R	Stannylalkene consumed (%)	% Yield of adduct	% Yield of hydrol. prod.	B.p. or m.p. (°C)
Me	100	73[a]	0	113–117/0.005
Et	100	21[b]	0	115–120/0.005
Et	90	0	90[c]	
Et	0[d]	0	0	
Ph	100	66[b]	2	117–119
Ph	100	69[e]	5	
PhCH=CH	95	51[b]	5	104–106
PhCH=CH	100	68[f]	3	
PhCH=CH	100	70[g]	10	

[a] Before distillation. [b] Yield of isolated product. [c] Work-up at −30 °C, 10% $(EtCHO)_3$ isolated. [d] Reaction carried out in ether. [e] Work-up without NH_4Cl, two products ($RSnMe_2OH : RSnMe_3$ = 55 : 45). [f] Work-up with NH_4Br: product of type $RSnMe_2Br$. [g] Work-up without NH_4Cl: two products ($RSnMe_2OH : RSnMe_3$ = 80 : 20).

Table 2

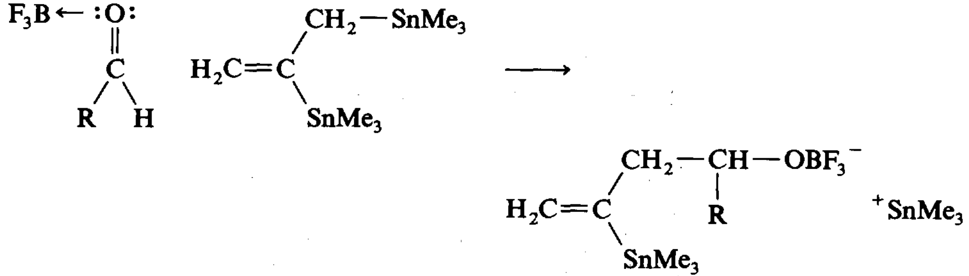
Tin-119 and carbon-13 NMR data (δ in ppm vs. internal Me_4Sn or TMS, J in Hz) for compounds of the type $H_2C^1{=}C^2(SnMe_2Cl)C^3H_2C^4H(OH)R$

R	$\delta^{119}Sn$	δC^1 ($^2J(SnC)$)	δC^2 ($^1J(SnC)$)	δC^3 ($^2J(SnC)$)	δC^4 ($^3J(SnC)$)	$\delta SnMe$ ($^1J(SnC)$)
Me	−20.76	128.42	149.62	46.47	69.05	1.37
		(35.6)	(648.5)	(63.6)	(10.2)	(479.4)
Et	−23.04	128.27	149.49	44.03	74.10	1.27
		(35.6)	(615.0)	(63.6)	(n.o.)	(478.1)
Ph	−5.67	128.80	150.05	47.77	75.40	1.13
		(33.1)	(634.5)	(61.0)	(7.6)	(463.8)
Ph [a]	ca. −33.00	128.78	150.82	47.14	76.58	−1.30
		(32.0)	(633.2)	(58.7)	(n.o.)	(458.5)
PhHC=CH	−10.05	129.05	149.05	45.49	73.88	1.11
		(33.1)	(653.1)	(61.0)	(10.2)	(472.0)
PhHC=CH [b]	−18.41	129.91	148.42	45.50	73.91	1.93
		(n.o.)	(615.4)	(61.0)	(n.o.)	(460.3)
PhHC=CH [a]	ca. −32.00	127.88	149.05	44.93	73.44	−0.59
		(n.o.)	(673.8)	(n.o.)	(n.o.)	(493.8)

[a] Organotin residue $SnMe_2OH$. [b] Organotin residue $SnMe_2Br$; n.o. = not observed.

Homoallylic alcohols were readily characterised by NMR spectroscopy (data are listed in Tables 2 and 3); their IR spectra showed the OH stretching frequency at ca. 3350 cm^{-1}). Mass spectrometric studies were also carried out. The molecular ions were not observed, but (as is usual for trimethyltin compounds) the fragment ions corresponding to loss of one methyl group were always present, although at low peak intensities. These fragment ions subsequently lose the aldehyde moiety (possibly via a McLafferty rearrangement): peaks corresponding to RCHO were the base peaks in the case of benzaldehyde and cinnamaldehyde.

The mechanism of the Lewis acid-catalysed addition of allyltins to aldehydes is well established [13]; the aldehyde, activated by complexation with the Lewis acid $BF_3 \cdot Et_2O$, attacks the allyltin with allylic inversion:



The ion pair formulation is due to Tagliavini [8]; Denmark has established by NMR studies that a tin alkoxide is not formed [21].

A temperature-dependent NMR study of the present reaction with acetaldehyde established the following facts: (a) At −43°C the aldehyde is present as the trimer, while the organotin reagent remains unchanged; (b) At room temperature the tin-119 NMR spectrum shows the presence of only tetramethyltin and a second,

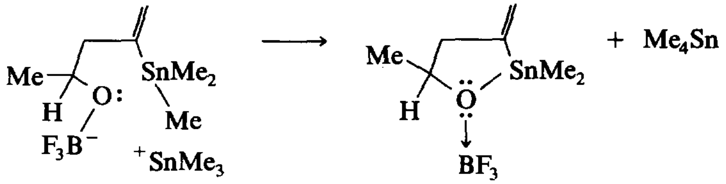
Table 3

Structure-relevant ^1H chemical shifts and coupling constants for compounds of the type $H_2C{=}C(SnMe_2Cl)CH_2CH(OH)R$

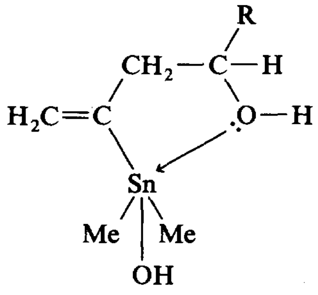
R	$\delta H_{vin,c}$ $^nJ(HH)$	$^3J_c(SnH)$	$\delta H_{vin,tr}$ $^nJ(HH)$	$^3J_{tr}(SnH)$	$\delta H_{all}(1)$ $^nJ(HH)$	$\delta H_{all}(2)$ [a] $^nJ(HH)$	$\delta CHOH$ $^nJ(HH)$	δOH	$\delta SnMe_2Cl$
Me	5.84(m)	102.0	5.94(m)	216.0	2.36(dd) 14.4/8.6	2.64(dd) 14.4/3.2	3.91(m)	2.50	0.63(s)
Et	5.92(m)	104.0	6.07(m)	212.0	3.52(d) 3.2	–	3.72(m)	2.60	0.73(s)
Ph	5.83(m)	95.6	5.94(m)	215.0	2.71(m)	–	4.66(m)	3.12	0.69(s)
Ph [b]	5.78(m)	147.1	5.82(m)	213.3	2.68(m)	–	4.65(m)	2.53	0.51(s)
PhHC=CH	5.88(m)	99.3	5.98(m)	211.8	2.61(dd) 14.5/8.8	2.77(dd) 14.5/2.6	4.36(m)	2.58	0.68(s)
PhHC=CH [c]	5.93(m)	97.8	5.99(m)	210.3	2.63(dd) 15.3/8.6	2.77(dd) 15.3/3.2	4.35(m)	1.65	0.78(s)
PhCH=CH [b]	5.50(m)		5.89(m)		2.53(m)	2.68(m)	4.36(m)	1.72	0.57(s)

[a] Nonisochronicity of the allyl protons results in an ABX spin system. [b] Organotin residue $SnMe_2OH$. [c] Organotin residue $SnMe_2Br$.

broad, signal at ca. +42 ppm. A subsequent GLC study made it clear that Me_4Sn is formed quantitatively. This shift suggests the presence of an Sn–O linkage [22] and indicates the following reaction step:



The reaction with benzaldehyde gives a similar result, the signal attributed to the cyclic tin alkoxide occurring at +55 ppm. Hydrolysis will presumably afford a tin hydroxide, which undergoes anion exchange with the ammonium salt to give the final product; the tin hydroxide is, in fact, obtained when the hydrolysis is carried out in the absence of NH_4X.



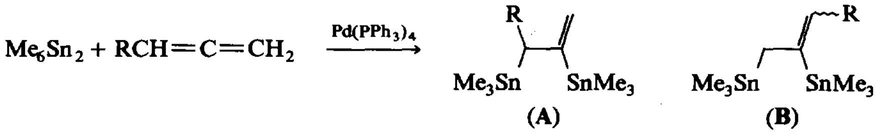
(R = Ph, PhCH=CH)

The tin-119 signals from the product tin chlorides and bromides also occur at negative values (−6 to −23 ppm), so that it is clear that in all these species the tin has a coordination number of 5. Carbon-13 data support this postulate.

Formation of the "hydrolysis product", isopropenyltrimethyltin, occurs when the distannylpropene is subjected to the complete reaction procedure in the *absence* of an aldehyde; its formation as a by-product when aldehyde is present is probably due to incomplete dissociation of the aldehyde trimer before hydrolysis is carried out. This is supported by the higher yield of isopropenyltrimethyltin when acetaldehyde or propionaldehyde is used. The allylic tin residue removed by hydrolysis is detected as trimethyltin chloride.

Reactions of substituted distannylpropenes

The reaction of hexamethylditin with an allene $RCH=C=CH_2$ can give up to 3 products:



Of these, **A** is the kinetic product and **B** (which can exist as an *E*/*Z* mixture) the thermodynamic product.

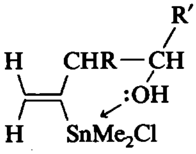
Table 4

Change in isomer distribution when distannylalkenes **A**/**B** are treated with $BF_3 \cdot Et_2O$ at −43° C

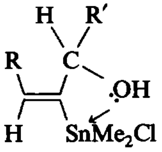
R	Initial ratio [a]			Final ratio [a]		
	E-**B**	*Z*-**B**	**A**	*E*-**B**	*Z*-**B**	**A**
Ph	47	53	0	75	25	0
Bu	82	15	3	60	40	0
^{c}Hex	11	2	87	50	50	0
^{t}Bu	6	1	93	20	80	0

[a] From GLC measurements.

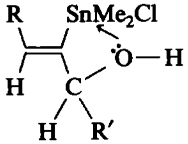
When such a mixture of isomers **A** and **B** is allowed to react with an aldehyde R′CHO, four products can arise. In all cases studied there is a halodemethylation at the vinylic tin centre, as described above:



(*erythro*/*threo*-**C**)



(*E*-**D**)



(*Z*-**D**)

The question arises as to which precursor (**A**/**B**) is responsible for the products **C**/**D**, since allylic 1,3-shifts of organotin moieties are well known [23,24]. $BF_3 \cdot Et_2O$ catalyses the equilibrium between **A** and **B**.

We carried out NMR measurements on the system distannylalkene/acetaldehyde/$BF_3 \cdot Et_2O$ at −43° C. No reaction apart from aldehyde trimerisation occurred, but the ratios of **A** and **B** changed considerably (see Table 4). It thus

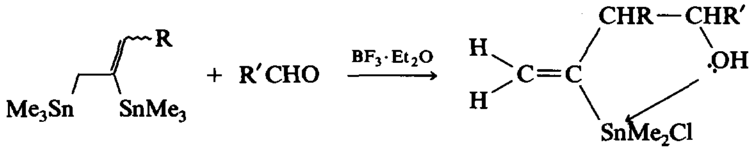
Table 5

Products obtained from reactions between substituted 2,3-bis(trimethylstannyl)-1-propenes and aldehydes R′CHO

Subst. R	R′	Yield (%)	Relative isomer ratios			Hydrolysis product (%)
			C	*E*-**D**	*Z*-**D**	
Bu	Me	75	61:34	5		3
Bu	Ph	89 [a]	58:42			0
^{t}Bu	Me	75 [b]	84:16			6
^{t}Bu	Ph	75	30	70		11
^{c}Hex	Me	44	91	9		44
^{c}Hex	Ph	94 [c]	70	30		3
^{c}Hex = [d]	Me	20	100			10
^{c}Hex = [d]	Ph	78 [e]	100			5
^{c}Non [f]	Me	71 [g]	100			7
^{c}Non [f]	Ph	67 [g]	80:20			4
EtO_2CCH_2	Ph	74	60:40			

[a] M.p. 152–154° C. [b] M.p. 187–189° C. [c] M.p. 168–170° C. [d] Cyclohexylidene. [e] Ca. 30% cyclo-$C_5H_{10}C{=}C(CMeOH)CH{=}CH_2$ formed. [f] 1,2-Cyclononadiene/ditin adduct; [g] *E*-Configuration at the double bond. Relative isomer ratios for **C** are stated without assignment as *erythro* or *threo*.

seems safe to assume that products **C** and **D** are derived solely from *E*- and *Z*-**B**; in the absence of $BF_3 \cdot Et_2O$ the **A**/**B** ratios are unchanged. Since we can assume that the reaction between the allyltin and aldehyde proceeds with allyl inversion [2], we can expect only *erythro*- and *threo*-**C** to be formed:



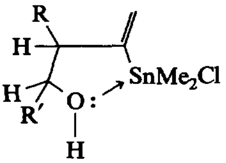
(C)

Intramolecular coordination will favour the formation of certain rotamers of **C** (see below). The results of the reactions carried out are summarised in Table 5, product NMR data in Tables 6 and 7. Although **C** is indeed generally the sole product there are exceptions, and it may on occasion even be the minor product. The nature of the aldehyde also appears to play a role in product determination.

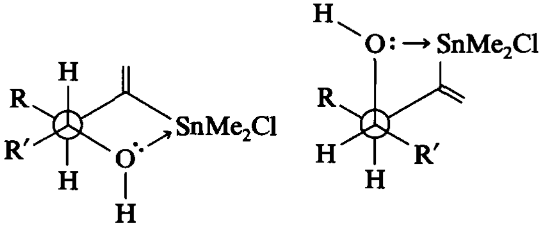
A "hydrolysis product" is again formed and is always of the type $H_2C{=}C(SnMe_3)CH_2R$, i.e. it is formed with allyl inversion. Minor amounts of other by-products are also formed in certain cases.

Absolute configuration of C

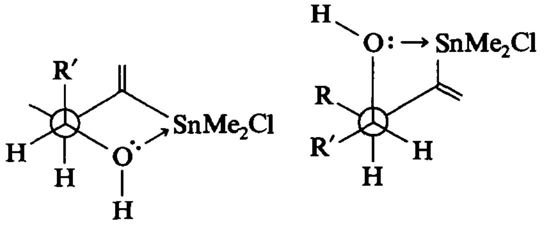
Previous work on the reactions between allyltins and aldehydes has indicated an *erythro*-selectivity [13]. In order to determine whether this is also true for the present system, we must determine the exact geometry of the two isomers of **C** formed. This can apparently most readily be done by use of the values of $^3J(H,H)$ for



However, as mentioned above, the pentacoordination in **C** will permit only the following rotamers to coexist:



threo



erythro

Table 6

Tin-119 and carbon-13 NMR data (δ in ppm vs. internal Me_4Sn or TMS, J in Hz) for compounds of the type $H_2C^1{=}C^2(SnMe_2Cl)C^3HR^1C^4H(OH)R^2$ (**C**) and E/Z-$R^1HC^1{=}C^2(SnMe_2Cl)C^3H_2CH(OH)R^2$ (**D**)

R^1	C/D	R^2	$\delta^{119}Sn$	δC^1 ($^2J(SnC)$)	δC^2 ($^1J(SnC)$)	δC^3 ($^2J(SnC)$)	δC^4 ($^3J(SnC)$)	$\delta Sn\mathit{Me}$ ($^1J(SnC)$)
^{n}Bu	*E*-**D**	Me	−21.85	143.69 (n.b.)	137.39 (n.b.)	39.05 (40.6)	68.94 (17.8)	1.51 (n.o.)
	C-1	Me	−29.17	127.11 (35.6)	154.08 (656.1)	51.91 (53.4)	71.44 (10.2)	1.77 (474.0)
	C-2	Me	−37.21	129.45 (35.6)	152.07 (653.6)	56.05 (53.4)	71.70 (n.o.)	2.29 (n.o.)
^{n}Bu	**C**-1	Ph	−23.89	129.18 (31.0)	155.03 (640.8)	54.62 (53.4)	77.42 (n.o.)	2.09 (460.0)
	C-2	Ph	−15.05	128.07 (31.0)	151.65 (658.6)	55.09 (53.4)	77.42 (n.o.)	1.65 (456.0)
^{t}Bu	**C**-1	Me	−37.70	130.13 (33.1)	152.55 (668.8)	61.28 (50.9)	72.13 (12.7)	2.36 (470.0)
	C-2	Me	−49.52	134.14 (33.1)	149.06 (679.0)	63.72 (50.9)	68.06 (n.o.)	3.29 (n.o.)
^{t}Bu	*E*-**D**	Ph	7.47	134.54 (n.o.)	142.82 (653.0)	50.09 (56.0)	76.43 (n.o.)	3.13 (455.0)
	C	Ph	−11.91	129.14 (n.o.)	153.10 (n.o.)	53.93 (n.o.)	78.72 (n.o.)	1.97 (n.o.)
^{c}Hex	*E*-**D**	Me	−40.73	151.00 (43.2)	136.69 (602.0)	46.86 (59.7)	69.81 (n.o.)	1.55 (476.0)
	C	Me	−38.22	128.36 (33.0)	152.08 (644.0)	56.32 (50.8)	70.46 (n.o.)	1.55 (476.0)

^{c}Hex	*E*-D	Ph	−1.06	151.49	136.78	47.79	76.30	1.12
				(40.7)	(597.6)	(48.5)	(n.o.)	(n.o.)
	C	Ph	−19.25	129.87	153.33	59.57	78.06	1.77
				(33.1)	(653.6)	(50.9)	(12.7)	(450.0)
^{c}Hex =	C	Me	−46.45	126.37	157.22	47.03	77.50	2.86
				(35.6)	(681.6)	(48.3)	(n.o.)	(480.7)
^{c}Hex =	C	Ph	−39.32	117.38	157.93	47.55	80.62	2.80
				(38.1)	(695.7)	(45.8)	(n.o.)	(452.7)
^{c}Non [a]	C-1	Me	−26.29	140.98	145.16	43.83	71.64	2.00
				(33.1)	(676.5)	(55.9)	(17.8)	(467.9)
	C-2	Me	−38.71	140.78	144.10	45.83	71.76	2.75
				(n.o.)	(n.o.)	(n.o.)	(n.o.)	(n.o.)
^{c}Non [a]	C	Ph	−14.25	142.38	144.35	45.43	77.15	1.88
				(28.0)	(663.8)	(53.4)	(17.8)	(465.4)
Ph	*E*-D	Me	−23.92	137.71	142.71	45.31	69.14	−1.46
				(n.o.)	(n.o.)	(51.4)	(n.o.)	(n.o.)
	C-1	Me	−25.94	130.02	152.53	58.58	71.53	2.10
				(35.6)	(653.6)	(58.6)	(12.7)	(475.6)
	C-2	Me	−33.99	125.94	153.29	59.71	72.14	2.10
				(35.6)	(658.7)	(61.0)	(n.o.)	(475.6)
CH_2COOEt	C-1	Ph	−31.35	128.47	150.78	50.48	76.34	1.55
				(33.1)	(661.2)	(58.6)	(n.o.)	(470.4)
	C-2	Ph	−19.04	128.90	152.87	51.11	75.49	1.53
				(30.6)	(638.4)	(53.4)	(n.o.)	(470.0)

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[a] Double bond geometry *E*; n.o. = not observed.

Table 7

Structure-relevant ^1H chemical shifts and coupling constants for compounds of the type $H_2C{=}C(SnMe_2Cl)CH_AR^1CH_B(OH)R^2$ (**C**) and *E/Z*-$R^1HC{=}C(SnMe_2Cl)CH_2CH(OH)R^2$ (**D**)

R^1	C/D	R^2	$\delta H_{vin,c}$ $^nJ(HH)$	$^3J_c(SnH)$	$\delta H_{vin,tr}$ $^nJ(HH)$	$^3J_{tr}(SnH)$	δH_{all} $^nJ(HH)$	$\delta CHOH$ $^nJ(HH)$	δOH	$\delta SnMe_2Cl$	$^3J(H_AH_B)$
^{n}Bu	*E*-**D**	Me	n.b.	n.o.	–	n.o.	2.75(dd) [a] 5.1/12.7	4.00(m)	2.68	0.67(s)	
	C-1	Me	5.90(m)	102.4	5.85(m)	223.8	2.38(m)	4.00(m)	2.64	0.61(s)	2.0
	C-2	Me	5.93(m)	99.1	5.87(m)	235.6	2.20(m)	4.00(m)	2.89	0.61(s)	2.0
^{n}Bu	C-1	Ph	5.95(m)	98.4	5.91(m)	215.9	2.63(m)	4.92(m)	2.67	0.76(s)	3.0
	C-2	Ph	5.87(m)	103.7	5.74(m)	214.6	2.60(m)	4.77(m)	2.92	0.68(s)	3.0
^{t}Bu	C-1	Me	6.06(m)	110.9	6.00(m)	233.8	2.34(d) 3.6	4.15(m)	2.92	0.57(s)	3.6
	C-2	Me	6.20(m)	117.5	5.97(m)	214.0	1.99(d) 1.5	4.47(m)	3.42	0.55(s)	1.5
^{t}Bu	*E*-**D**	Ph	6.23(s)	101.7	–		2.69(d) 8.3	4.66(t) 8.3	2.35	0.78(s)	
	C	Ph	6.06(d) 1.6	114.4	5.99(d) 1.6	221.1	2.79(d) 4.3	5.04(d) 4.3	2.57	0.82(s)	4.3
^{c}Hex	C	Me	6.03(s)	107.6	5.89(s)	230.4	2.33(dd) 6.1/6.1	4.11(m)	3.69	0.62(s)	6.1

^{c}Hex	*E*-D	Ph	6.04(m)	102.0	–	–	2.61(d) 7.0	4.64(t) 7.0	2.50	0.72(s)	
	C	Ph	6.04(d) 1.9	100.0	5.92(d) 1.9	209.4	2.55(dd) 4.1/4.1	4.95(d) 4.1	3.03	0.61(s)	4.1
^{c}Hex =	C	Me	6.12(d) 1.7	93.2	5.98(d) 1.7	231.0	–	4.75(m)	3.48	0.68(s)	
^{c}Hex =	C	Ph	6.09(s)	114.2	5.83(s)	239.5	–	4.72(s)	3.53	0.65(s)	
^{c}Non[b]	C-1	Me	6.39(t) 8.5	112.2	–		2.20(m)	3.82(m)	2.88	0.64(s)	
	C-2	Me	6.59(t) 8.5	112.9	–		2.20(m)	3.95(m)	3.14	0.60(s)	
^{c}Non[b]	C	Ph	6.52(t) 8.7	111.6	–		2.20(m)	4.88(m)	3.24	0.65(s)	
Ph	C-1	Me	6.09(s)	97.1	5.98(s)	214.6	3.43(d) 3.8	4.26(m)	2.96	0.76(s)	3.8
	C-2	Me	6.09(s)	97.1	5.61(s)	208.7	3.75(d)	4.16(m)	2.66	0.57(s)	7.2
CH_2COOEt	C-1	Ph	5.96(s)	95.6	5.81(s)	212.0	4.00(m)	4.69(d) 4.9	4.55	0.68(s)	4.9
	C-2	Ph	5.89(s)	100.4	5.97(s)	208.0	3.15(m)	4.87(d) 3.0	4.55	0.71(s)	2.9

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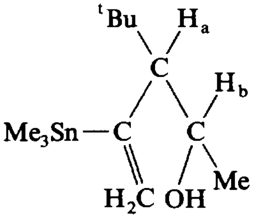
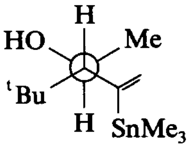
[a] Second allyl proton: 2.64 (dd: 14.4/3.2 Hz). [b] *E* Double bond configuration.

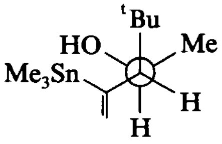
The relative positions of the hydrogen atoms would lead us to expect a greater value for ^3J(H,H) in the *threo* isomer (dihedral angles 180°, 60°) than in the *erythro* isomer (60°, 60°). However, the values obtained (Table 7) do not permit a clear determination of the product geometries, so that it is necessary to remove the pentacoordination. This can readily be done by treating the alcohols with an excess of methylmagnesium halide, thus converting $RSnMe_2X$ into $RSnMe_3$. The clearest case we were able to examine was that of



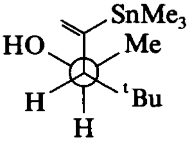
for which $^3J(H_a,H_b)$ was found to be 9.2 Hz in the major isomer and 2.6 Hz in the minor (isomer ratio 10:1). The former must be the *erythro* isomer, which will exist preferentially as the rotamer *e*-I, and the latter the *threo* isomer, which will prefer the form *t*-I.



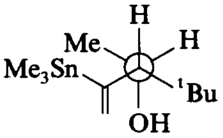
(*e*-I)



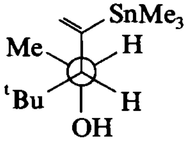
(*e*-II)



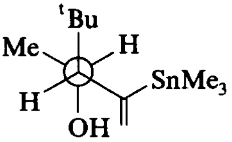
(*e*-III)



(*t*-I)



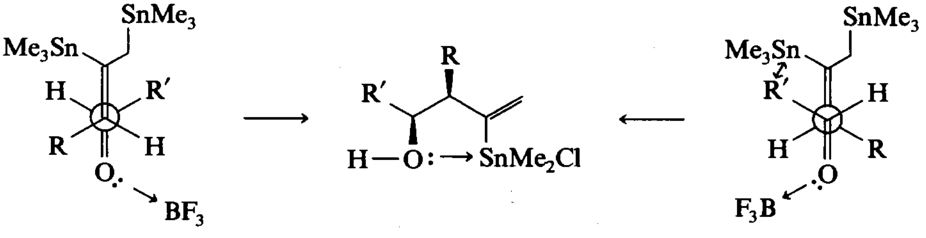
(*t*-II)



(*t*-III)

Thus the erythro-selectivity reported in the literature [13,19,20,25] is not affected by the presence of the second $SnMe_3$ group. Since in this clear case there is a tin chemical shift difference between the *erythro* (−37.7 ppm) and *threo* (−49.5 ppm) isomers of 12 ppm, and this has a similar magnitude for the other isomer pairs, we suggest tentatively that this shift difference can be used for isomer assignment.

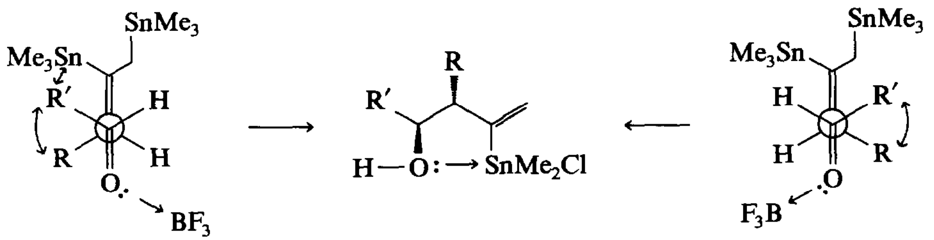
Following Yamamoto [13,26] we can postulate the following geometries as precursors for the *erythro* and *threo* isomers:



(Z_a)

erythro

(E_a)



(Z_b) *threo* (E_b)

The double-headed arrows indicate unfavourable steric interactions which will lead (a) to preferential formation of the *erythro* compound, and (b) to its possible preferential formation from the Z-isomer.

Experimental

All manipulations involving organotin compounds were carried out under argon. Allenes were prepared by literature procedures [27]. NMR spectra were recorded using a Bruker AM-300 spectrometer (solutions in $CDCl_3$, standards TMS and Me_4Sn). GLC analyses were carried out using Carlo Erba HRGC-5300 and HRGC-4160 instruments fitted with either 25 m CP-SIL-5 CB or 30 m DB1-(5)-CB quartz columns. Mass spectra were obtained using a Finnigan MAT 8230 instrument, IR spectra with a Perkin–Elmer model 577 spectrometer.

Reactions between the distannylalkenes and aldehydes were carried out as follows: The aldehyde (10 mmol; in the case of acetaldehyde 12 mmol) is treated with methylene chloride (20 mL). This solution is cooled to $-78\,^{\circ}C$; $BF_3 \cdot Et_2O$ (2.5 mL, 20 mmol) is added during 5 min, followed by a solution of the distannylalkene (10 mmol) in methylene chloride (30 mL) during 15 min. After 1 h the mixture is allowed to warm to room temperature; if an intense yellow colour is observed the reaction must be brought to a halt at once. Work-up is carried out by pouring the solution into 100 mL of a saturated solution of NH_4Cl/NH_4Br in water. The organic layer is separated and the aqueous layer extracted twice with 30 mL diethyl ether. The combined organic layers are dried over Na_2SO_4 and the solvents removed under pressure. By-products can be removed by dry column chromatography: a 60 cm length of chromatography tubing is filled with deactivated alumina. The product mixture is dissolved in methylene chloride (80 mL) and the solution added slowly to the column. When the solvent front has reached the lower end of the column, the tubing is illuminated with a UV lamp. The zones thus made visible are cut out with a knife and extracted with ether (2 × 50 mL). After removal of the solvent, the homoallylic alcohol (E/Z mixture) is at least 96% pure according to its proton NMR spectrum. This method does not permit E/Z isomer separation.

Solid products are recrystallised from a methylene chloride/ether mixture (1 : 3).

Acknowledgement

This work was supported by the Volkswagen Foundation and the Fonds der Chemischen Industrie.

References

1 W.P. Neumann and K. König, Tetrahedron Lett., (1967) 495.
2 C. Servens and M. Pereyre, J. Organomet. Chem., 26 (1971) C4.
3 C. Servens and M. Pereyre, J. Orgnaomet. Chem., 35 (1972) C20.
4 C.W. Fong and W. Kitching, J. Organomet. Chem., 22 (1970) 95 and 107.
5 Y. Yamamoto, H. Yatagai, Y. Ishihara and K. Maruyama, Tetrahedron, 40 (1984) 2239.
6 G. Tagliavini, Rev. Si, Ge, Sn, Pb Comp., 8 (1985) 237.
7 G.E. Keck, M.B. Andrus and S. Castellino, J. Am. Chem. Soc., 111 (1989) 8136.
8 S.E. Denmark and E.J. Weber, J. Am. Chem. Soc., 106 (1984) 7970.
9 J. Iqbal and S.P. Joseph, Tetrahedron Lett., 30 (1989) 2421.
10 G.E. Keck and D.E. Abott, Tetrahedron Lett., 25 (1984) 1883.
11 G.E. Keck and D.E. Abott, Tetrahedron Lett., 25 (1984) 3927.
12 S.E. Denmark, B.R. Henke and E.J. Weber, J. Am. Chem. Soc., 109 (1987) 2512.
13 Y. Yamamoto, Acc. Chem. Res. 20 (1987) 243.
14 C. Hull, S.V. Mortlock and E.J. Thomas, Tetrahedron 45 (1989) 1007.
15 J.P. Quintard, G. Dumartin, B. Elissondo, A. Rahm and M. Pereyre, Tetrahedron, 45 (1989) 1017.
16 J.A. Marshall and W.Y. Gung, Tetrahedron, 45 (1989) 1043.
17 S.E. Denmark, E.J. Weber, T.M. Wilson and T. Willson, Tetrahedron, 45 (1989) 1053.
18 T.N. Mitchell and H. Killing, Organometallics, 3 (1984) 1318; T.N. Mitchell and U. Schneider, J. Organomet. Chem., 407 (1991) 319.
19 A. Boaretto, D. Marton and G. Tagliavini, J. Organomet. Chem. 321 (1987) 199.
20 Y. Yamamoto, H. Yagatai, Y. Naruta and K. Maruyama, J. Am. Chem. Soc., 102 (1980) 7107.
21 S.E. Denmark, T.M. Wilson and T. Willson, J. Am. Chem. Soc., 110 (1988) 984.
22 B. Wrackmeyer, Ann. Rep. NMR Spectrosc., 16 (1985) 73.
23 J.P. Quintard and M. Pereyre, J. Org. Chem., 48 (1983) 1559.
24 J.A. Marshall and W.Y. Gung, Tetrahedron Lett., 30 (1989) 2183.
25 L. Brandsma and H.D. Verkruijsse, Synthesis of Allenes, Acetylenes and Cumulenes, Studies in Organic Chemistry, Vol. 8, Elsevier Amsterdam, 1981.
26 Y. Yamamoto, Rev. Si, Ge, Sn, Pb Comp., 9 (1986) 279.